

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/034449 A2

(51) International Patent Classification⁷: **H01L 21/20**

(21) International Application Number:
PCT/US2003/032439

(22) International Filing Date: 10 October 2003 (10.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/417,767 11 October 2002 (11.10.2002) US

(71) Applicant (for all designated States except US): **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CARCIA, Peter, Francis** [US/US]; 3413 Sweet Briar Road, Wilmington, DE 19810 (US). **MCLEAN, Robert, S.** [US/US]; 208 Eileen's Way, Hockessin, DE 19707 (US).

(74) Agent: **SIEGELL, Barbara, C.**; E.I. Dupont De Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

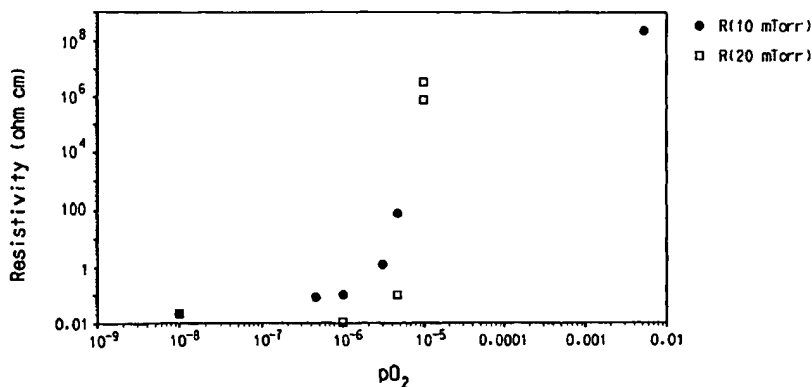
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TRANSPARENT OXIDE SEMICONDUCTOR THIN FILM TRANSISTORS



(57) Abstract: This invention relates to novel, transparent oxide semiconductor thin film transistors (TFT's) and a process for making them.

WO 2004/034449 A2

TITLE

TRANSPARENT OXIDE SEMICONDUCTOR THIN FILM TRANSISTORS

FIELD OF THE INVENTION

5 The present invention relates to a transistor fabricated with a transparent oxide semiconductor selected from the group consisting of zinc oxide, indium oxide, tin oxide, and cadmium oxide deposited without the intentional incorporation of additional doping elements and the process for deposition of the oxide semiconductors. Transparent oxide
10 semiconductors are useful in fabrication of transparent thin film transistors. Transparent transistors can be used to control pixels in a display. By being transparent, the transistor may not significantly reduce the active area of the pixel.

TECHNICAL BACKGROUND

15 Fortunato et al (Materials Research Society Symposium Proceedings (2001) 666) described zinc oxide films containing aluminum deposited on polyester by radio-frequency magnetron sputtering.

 Japanese Patent Application 2002076356 A describes a channel layer made of zinc oxide and doped with transition metals.

20 Goodman (US 4204217 A) discloses a liquid crystal transistor.

 Ohya et al (Japanese Journal of Applied Physics, Part 1 (Jan. 2001) vol 40, no.1, p297-8) disclose a thin film transistor of ZnO fabricated by chemical solution deposition.

25 Maniv et al (J. Vac. Sci Technol., A (1983), 1(3), 1370-5) describe conducting zinc oxide films prepared by modified reactive planar magnetron sputtering.

 Giancaterina et al (Surface and Coatings Technology (2001) 138(1), 84-94) describe zinc oxide coatings deposited by radio frequency magnetron sputtering.

30 Seager et al. (Appl. Phys. Lett. 68, 2660-2662, 1996) describe using the electric field emanating from a ferroelectric insulator to control or modulate resistance in a conducting film of ZnO:Al or ZnO:In.

 Transparent conducting oxides are reviewed in the August, 2000 issue of the Materials Research Bulletin, Volume 25 (8) 2000, devoted to
35 materials and properties of transparent conducting oxide compounds.

SUMMARY OF THE INVENTION

This invention relates to novel, transparent oxide semiconductor (TOS) thin film transistors (TFT's) and the process for their deposition, where the transparent oxide semiconductor (TOS) is selected from the group consisting of zinc oxide (ZnO), indium oxide (In₂O₃), tin oxide (SnO₂), or cadmium oxide (CdO) semiconductor and combinations thereof. The TFT structure described includes the TOS with conducting electrodes, commonly referred to as a source and a drain, for injecting a current into the TOS and a capacitance charge injection scheme for controlling and/or modulating the source-drain current. The semiconductor deposition process uses magnetron sputtering of an oxide (ZnO, In₂O₃, SnO₂, CdO) or metal (Zn, In, Sn, Cd) target in an atmosphere with a controlled partial pressure of oxygen in an inert gas. This is a low temperature process which is compatible with temperature sensitive substrates and components. One particularly attractive application of TOS TFT's is in the drive circuits for displays on flexible, polymer substrates.

The process specifically involves depositing an undoped transparent oxide semiconductor in a field effect transistor, comprising a method selected from the group consisting of:

- a) physical vapor deposition of undoped TOS in an effective partial pressure of oxygen mixed with an inert gas;
- b) resistive evaporation of undoped TOS in an effective partial pressure of oxygen;
- c) laser evaporation of undoped - TOS in an effective partial pressure of oxygen;
- d) electron beam evaporation of undoped TOS in an effective partial pressure of oxygen; and
- e) chemical vapor deposition of undoped TOS in an effective partial pressure of oxygen.

The invention also concerns a transistor comprising with an undoped transparent oxide semiconductor. In one embodiment the transistor is on a flexible substrate and further comprises a gate dielectric fabricated from

a material selected from the group consisting of zinc oxide, indium oxide, tin oxide, and cadmium oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the dependence of resistivity on pO_2 for ZnO films rf magnetron sputtered in 10 mTorr and 20 mTorr of argon and oxygen.

Figure 2 shows the general resistance characteristic as a function of the partial pressure of the oxygen source for ZnO films made by PVD or CVD methods.

Figure 3 shows the ZnO TFT test configuration.

Figure 4 shows a ZnO TFT I-V curve for rf (radio frequency) magnetron sputtered films made with $pO_2 = P_c$

Figure 5 shows a ZnO TFT I-V curve for rf magnetron sputtered films made with $pO_2 = 2P_c$

Figure 6 shows a ZnO TFT I-V curve for rf magnetron sputtered films made with $pO_2 = 0.75P_c$

Figure 7 shows a ZnO TFT I-V curve for rf magnetron sputtered films made with $pO_2 = 0.08P_c$

Figure 8 shows a ZnO TFT I-V curve for rf magnetron sputtered films made with $pO_2 = 20P_c$

Figure 9 (a) and (b) show a I-V curve for ZnO TFT fabricated on a flexible substrate. Figure 9 (a) shows a curve of I_d versus V_d varying the gate voltage from 0V to 20V in steps of 1V. Figure 9(b) shows I_d versus gate voltage as $V_d = 20V$. In this transistor, $W = 400 \mu m$ and $L = 40 \mu m$.

Figure 10 shows optical images of a TFT comprised of only ZnO.

Figure 11 shows I-V curve for a TFT comprised of only ZnO.

Figure 12 shows I-V curve for a indium oxide TFT fabricated with pO_2 near P_c .

Figure 13 shows a graph of transistor current (I_d) versus drain voltage (V_d) curves for gate voltages between zero and three (3) volts and V_d between 0 and 3 V.

DETAILED DESCRIPTION

While most electronic devices are fabricated today on rigid substrates, such as single crystalline Si or glass, there is a growing interest in devices on plastic or flexible substrates, particularly because they would be more mechanically robust, lighter weight, and potentially cheaper to manufacture by roll-to-roll processing. However, plastic substrates, such as polyethylene terephthalate (e.g., Mylar[®], E. I. DuPont

de Nemours Inc., and Wilmington, DE) limit device processing to below 100 C. One consequence is that electronics based on Si, even amorphous Si, is incompatible with temperature-sensitive plastic substrates. This has fueled a broad interest in organic semiconductors as a low temperature class of alternative materials. However, most organic semiconductors generally have inferior electronic properties, compared to amorphous Si, for device application. Further, organic materials commonly degrade in normal atmospheric conditions, requiring protection strategies. In contrast a stable inorganic semiconductor with processing compatible with temperature-sensitive substrates, and electronic properties equivalent to amorphous Si would enable electronics for a variety of flexible substrates. For this application thin film transistors based on novel sputtered transparent oxide semiconductors can be made with excellent electronic properties on flexible substrates. The TOS is also transparent in the visible part of the electromagnetic spectrum. This may be of particular advantage (1) in electronic display applications.

As an example, magnetron sputtering is used to form the ZnO semiconductor layer. Using a unique range of deposition conditions, with no intentional substrate heating (compatible with low temperature plastic substrates), novel ZnO layers were made that were polycrystalline (X-ray diffraction) with good electron transport properties. The ZnO layers are suitable for application as semiconductors in TFTs.

The good transport characteristics of the ZnO semiconductor of this invention, and prototypical of these TOS, include high electrical resistivity, for low device 'off' current combined with high charge carrier mobility for high 'on' device current. In the sputtered ZnO thin films of the present invention, the electrical resistivity is controlled by metering the partial pressure of oxygen during deposition. A novel aspect of our preparation of ZnO was the discovery that sputtering conditions favorable for achieving low ZnO film stress were also favorable for high transconductance and high on/off current ratio in ZnO TFT devices made at room temperature. It is believed the reason is that low stress ZnO films have fewer defects and

a favorable electronic structure, which promote higher charge carrier mobility. Consequently, the ZnO films of the present invention exhibit better TFT device performance.

In one embodiment of this invention, the source, drain, and gate electrodes are resistance evaporated Al about 100 nm thick. The ZnO semiconductor is about 100 nm thick layer made by rf magnetron sputtering in a mixture of Ar and O₂ gases. The gate insulator is Al₂O₃, e-beam vapor-deposited with thickness between 100 nm and 300 nm. The substrates are polyethylene terephthalate (PET and Kapton® polyimide, E. I. DuPont de Nemours Inc., Wilmington, DE). All depositions were carried out, while maintaining the substrate at or near room temperature.

A thin film transistor (TFT) is an active device, which is the building block for electronic circuits that switch and amplify electronic signals. Attractive TFT device characteristics include a low voltage to turn it on, a high transconductance or device current / (gate) control voltage ratio, and a high 'on' ($V_g > 0$) current to 'off' ($V_g \leq 0$) current ratio. In a typical TFT structure of this invention, the substrate is paper or polymer, such as PET, PEN, Kapton, etc. Source and drain conducting electrodes are patterned on the substrate. The TOS is then deposited, followed by a gate insulating layer such as SiO₂ or Al₂O₃. Finally, a gate conducting electrode is deposited on the gate insulating layer. One of skill in the art will recognize, this is one of many possible TFT fabrication schemes. In the operation of this device, a voltage applied between the source and drain electrodes establishes a substantial current flow only when the control gate electrode is energized. That is, the flow of current between the source and drain electrodes is modulated or controlled by the bias voltage applied to the gate electrode. The relationship between material and device parameters of the TOS TFT can be expressed by the approximate equation,

30

$$I_{sd} = (W/2L) C \mu (V_g)^2$$

where I_{sd} is the saturation source-drain current, C is the geometric gate capacitance, associated with the insulating layer, W and L are physical device dimensions, μ is the carrier (hole or electron) mobility in the TOS, and V_g is the applied gate voltage. Ideally, the TFT passes current only when a gate voltage of appropriate polarity is applied. However, with zero gate voltage the "off" current between source and drain will depend on the intrinsic conductivity,

$$\sigma = nq\mu$$

of the TOS, where n is the charge carrier density, and q is the charge, so that

$$(I_{sd}) = \sigma (Wt/L) V_{sd} @ V_g = 0$$

Here t is the TOS layer thickness and V_{sd} is the voltage applied between source and drain. Therefore, for the TFT to operate as a good electronic switch, e.g. in a display, with a high on/off current ratio, the TCOS semiconductor needs to have high carrier mobility but very small intrinsic conductivity, or equivalently, a low charge carrier density. On/off ratios $> 10^3$ are desirable for practical devices.

Specifically, when undoped ZnO thin films are dc or rf magnetron sputtered from a Zn or ZnO target in a partial pressure of oxygen, pO_2 , the bulk resistivity (R) changes abruptly from strongly semi-conducting ($R \sim 10^2$ ohm cm), to nearly insulating ($R \sim 10^6$ - 10^8 ohm cm), with increasing pO_2 . This dependence of R on pO_2 for ZnO films rf magnetron sputtered from an undoped ZnO target is shown in Figure 1. (The dependence of R on pO_2 will be similar for indium oxide, tin oxide, and cadmium oxide thin films). The sputtering system consisted of a cryo-pumped stainless steel vacuum chamber (about 25 inch diameter x 15 inch high) with a water-

cooled stationary table for substrates. The target diameter was 6.5 inches, the substrate-to-target distance was about 3 inches, and rf (13.56 MHz) power was coupled to the target through a standard impedance matching network. The vendor analysis of the target indicated it contained impurities of As, Fe, Cd, Cu, Ca, Mn, Na, Pb in amounts < 20 ppm. For the ZnO films whose resistivities are given in Figure 1, there is a critical oxygen partial pressure, P_c , for which the change in resistivity, ΔR_c in the vicinity of P_c is very large and abrupt. P_c is defined as the oxygen partial pressure corresponding to the mid point of the abrupt rise in resistivity. Specifically, ΔR_c increased by $>10^4$ ohm cm for pO_2 between $P_c/2$ and $2P_c$. For Figure 1, the critical pressure, P_c is approximately 10^{-5} Torr. This characteristic of an abrupt, large change in R versus pO_2 , occurring at a critical oxygen partial pressure P_c is a general result, as sketched in Figure 2, for ZnO films and other TOS films prepared by any vapor deposition method, chemical or physical, that requires a source of oxygen for the synthesis. Physical vapor deposition (PVD) principally involves all forms of sputtering (rf, dc, magnetron, diode, triode, ion-beam) and evaporation (resistive, laser, electron beam). Commonly PVD of TOS relies on a solid or molten source of the corresponding metal or metal oxide.. Chemical vapor deposition (CVD) requires chemical vapor transport and chemical reaction for film formation. Reactants are commonly gaseous, and examples of reaction types include pyrolysis, reduction, oxidation, disproportionation, and compound formation. CVD processes include low-pressure (LPCVD), plasma-enhanced (PECVD), atomic layer chemical vapor deposition (ALCVD, also known as atomic layer deposition, ALD), and laser-enhanced (LECVD) methods.

Independent of preparation method, P_c defines oxide growth conditions, for which the arrival rate of atomic oxygen just matches the arrival rate of atomic Zn, In, Sn, or Cd to form the stoichiometric oxide, e.g. ZnO, with semi-insulating resistivity, i.e. $\sim 10^8$ ohm cm. Consequently, only a small deviation from stoichiometry e.g., $Zn_{1.0001}O_{1.0000}$, will reduce the resistivity by orders of magnitude, since 0.01% excess Zn corresponds to $\sim 10^{19}$ free electrons (two electrons per interstitial Zn ion) or a resistivity ~ 1

ohm cm for $\mu \sim 1 \text{ cm}^2/\text{V-s}$. Therefore, in the vicinity of P_c , only a very small change in $p\text{O}_2$ will cause a large, abrupt change in resistivity, independent of the preparation method.

However, the actual value of P_c will depend on specific deposition conditions and the specific oxide as well as the physical and dynamic characteristics of the deposition system. Also, the actual magnitude of the resistance change, ΔR_c in the vicinity of P_c , will depend on the level of impurities (dopants) incorporated into the oxide film. A lower impurity level will increase the magnitude of ΔR_c , whereas a higher concentration of impurities will reduce it. But the general resistance characteristic will be system invariant, so that one skilled in the art of vapor deposition can find P_c for that particular system used to make undoped TOS films.

The field effect transistors of the present invention based on a nominally undoped TOS must be deposited under an effective partial pressure of oxygen using physical vapor deposition or chemical vapor deposition, preferably rf magnetron sputtering. An effective partial pressure of oxygen is a range of oxygen partial pressure about the critical partial pressure such that the electrical resistivity is intermediate between a low, nearly-conductive value observed for very low oxygen partial pressures and a high, nearly-insulating value observed for high oxygen partial pressures. The best performance (high channel current and high device on/off ratio) occurs when a TOS is made by vapor deposition in the preferable range of oxygen partial pressure, $0.1 P_c < p\text{O}_2 < 10 P_c$, and more preferably in the range, $0.5 P_c < p\text{O}_2 < 2 P_c$. The following examples of magnetron sputtered ZnO thin film transistors and an In_2O_3 TFT illustrate this effect. Conditions for ZnO preparation with $p\text{O}_2$ in the range $0.1 P_c < p\text{O}_2 < 10 P_c$, where $P_c \approx 10^{-5}$ Torr were chosen for sputtering in Examples 1-3. Examples 4 and 5 illustrate that sputtering outside the preferred $p\text{O}_2$ produces TFTs with inferior properties. Example 6 illustrates the structure and properties of a ZnO TFT fabricated on a flexible substrate. Example 7 illustrates properties of a ZnO TFT comprised of conducting ZnO source, drain, and gate electrodes, semiconducting ZnO channel, and a ZnO dielectric. Example 8 describes

properties of an indium oxide TFT made near the critical oxygen partial pressure.

The general structure of the ZnO and In_2O_3 field effect transistor of these examples is shown in Figure 3. TFTs were fabricated on heavily
5 doped n-type Si substrates with a thermal oxide layer about 100 nm thick on one side. Ti-Au source and drain electrodes (10 nm Ti followed by 100 nm Au), 200 μm wide with a 20 μm gap were deposited and patterned directly on the thermal silicon oxide layer by traditional photolithography. Ti-Au was also deposited on the back-side of the Si as a common gate
10 electrode, and ZnO or In_2O_3 about 100 nm thick was then sputtered between source and drain electrodes using a shadow mask.

The TFT structure described herein includes a transparent oxide semiconductor with conducting electrodes, commonly referred to as a source and a drain, for injecting a current into the oxide semiconductor
15 and a capacitance charge injection scheme for controlling and/or modulating the source-drain current. The semiconductor deposition process uses magnetron sputtering of an oxide or metal target in an atmosphere with a controlled partial pressure of oxygen in an inert gas. This is a low temperature process which is compatible with temperature
20 sensitive substrates and components. One particularly attractive application of TOS TFT's is in the drive circuits for displays on flexible, polymer substrates. TOS transistors and/or transistor arrays are useful in applications including, but not limited to, flat panel displays, active matrix imagers, sensors, rf price labels, electronic paper systems, rf identification
25 tags and rf inventory tags.

The TFT structure described herein is applicable to flexible substrates. The flexible substrate may be a polymer film such as, but not limited to, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyethersulphone (PES) and polycarbonate (PC). Flexible
30 substrates can also be thin metal foils such as stainless steel provided they are coated with an insulating layer to electrically isolate the thin film transistor.

By control of the oxygen partial pressure during deposition, it is possible to control the electrical conductivity of the undoped metal oxide such that the metal oxide can be an insulator, semiconductor or conductor.

Thus by varying the oxygen partial pressure, all elements of a thin film

- 5 transistor, semiconductor, conductors (source, drain and gate) and insulators (gate dielectric) can be made from the same oxide material but deposited under different conditions.

EXAMPLES

EXAMPLE 1

5 Using the transistor configuration shown in Fig. 3, a ZnO thin film semiconductor was rf magnetron sputtered at room temperature to deposit between source and drain electrodes, using a shadow mask. The ZnO target was 6.5 inch diameter and the rf power for sputtering was 100 W. The total gas pressure during sputtering was 20 mTorr, comprised of
10 1×10^{-5} Torr of oxygen, or $pO_2 = P_c$, with the balance being argon. The ZnO film thickness, determined optically, was 849 Å for a sputtering time of 500 sec. Fig. 4 is a set of corresponding drain current (I_d) versus drain voltage (V_d) transistor curves for gate voltages (V_g) between zero and 50 V. For this device, the field effect mobility (μ_{FE}) from the linear current-voltage
15 characteristics was determined to be $1.2 \text{ cm}^2/\text{V-s}$ with an on/off ratio equal to 1.6×10^6 . This on/off ratio corresponds to the ratio of source-drain current with 50 V and 0 V bias on the gate electrode while applying 10V between source and drain electrodes.

20

EXAMPLE 2

Using the transistor configuration shown in Fig. 3, a ZnO thin film semiconductor was rf magnetron sputtered at room temperature to deposit
25 between source and drain electrodes, using a shadow mask. The ZnO target was 6.5 inch diameter and the rf power for sputtering was 100 W. The total gas pressure during sputtering was 20 mTorr, comprised of 2×10^{-5} Torr of oxygen, or $pO_2 = 2P_c$, with the balance being argon. The ZnO film thickness, determined optically, was 677 Å for a sputtering time of 500
30 sec. Fig. 5 is a set of corresponding drain current (I_d) versus drain voltage (V_d) transistor curves for gate voltages (V_g) between zero and 50 V. For this device, the field effect mobility (μ_{FE}) from the linear current-voltage

characteristics was determined to be $0.3 \text{ cm}^2/\text{V-s}$ with an on/off ratio equal to 1.0×10^5 .

EXAMPLE 3

5 Using the transistor configuration shown in Fig. 3, a ZnO thin film semiconductor was rf magnetron sputtered at room temperature to deposit between source and drain electrodes, using a shadow mask. The ZnO target was 6.5 inch diameter and the rf power for sputtering was 100 W.

10 The total gas pressure during sputtering was 20 mTorr, comprised of 0.75×10^{-5} Torr of oxygen, or $p\text{O}_2 = 0.75 P_c$, with the balance being argon. The ZnO film thickness, determined optically, was 897 Å for a sputtering time of 500 sec. Fig. 6 is a set of corresponding drain current (I_d) versus drain voltage (V_d) transistor curves for gate voltages (V_g) between zero and 50

15 V. For this device, the field effect mobility (μ_{FE}) from the saturation current-voltage characteristics was determined to be $6.8 \text{ cm}^2/\text{V-s}$ with an on/off ratio equal to 1×10^3 .

EXAMPLE 4

20 Using the transistor configuration shown in Fig. 3, a ZnO thin film semiconductor was rf magnetron sputtered at room temperature to deposit between source and drain electrodes, using a shadow mask. The ZnO target was 6.5 inch diameter and the rf power for sputtering was 100

25 W. The total gas pressure during sputtering was 20 mTorr, comprised of 0.8×10^{-6} Torr of oxygen, or $p\text{O}_2 = 0.08 P_c$, with the balance being argon. The value $p\text{O}_2 = 0.08 P_c$ is outside our preferred range of oxygen partial pressure. The ZnO film thickness, determined optically, was 1071 Å for a sputtering time of 465 sec. Fig. 7 shows a set of the corresponding drain

30 current (I_d) versus drain voltage (V_d) curves for gate voltages (V_g) of zero, 30 V and 40 V. This device does not have the performance characteristics of a transistor. There is negligibly small modulation of the current by application of a gate voltage and the ratio of the device current with no

gate and either 30 or 40 V gate is unacceptably close to one. The device acts more like a resistor.

EXAMPLE 5

- 5 Using the transistor configuration shown in Fig. 3, a ZnO thin film semiconductor was rf magnetron sputtered at room temperature to deposit between source and drain electrodes, using a shadow mask. The ZnO target was 6.5 inch diameter and the rf power for sputtering was 100 W. The total gas pressure during sputtering was 20 mTorr, comprised of
- 10 2×10^{-4} Torr of oxygen, or $pO_2 = 20 P_c$, with the balance being argon. The value $pO_2 = 20 P_c$ is outside our preferred range of oxygen partial pressure. The ZnO film thickness, determined optically, was 1080 Å for a sputtering time of 465 sec. Fig. 8 shows a set of the corresponding drain current (I_d) versus drain voltage (V_d) curves for gate voltages (V_g) of zero to 50 V.
- 15 The device I-V curve is characteristic of a thin film transistor, however the drain current is quite small. For this device, the field effect mobility (μ_{FE}) from the linear current-voltage characteristics was determined to be 5×10^{-5} $cm^2/V\cdot s$ with an on/off ratio equal to about 700. Both the mobility and the on/off ratio are much smaller than for TFT devices made within the
- 20 preferred range of pO_2 .

EXAMPLE 6

- As an example of a ZnO TFT on a flexible substrate, transistors
- 25 were fabricated on DuPont Pyralux® (Cu-coated) polyimide. Cu source and drain were lithographically patterned using DuPont Riston® uv-imaged through a phototool, followed by sputtering 100 nm thick ZnO semiconductor. (The ZnO sputtering conditions were identical to those in Example 1). A fluoropolymer dielectric (relative dielectric constant, $\epsilon = 8.7$)
- 30 was then laminated at 120° C over the semiconductor active region, and Al gates were thermally evaporated using a shadow mask. Figure 9 (a) and (b) shows the performance of these flexible transistors, which have $\mu \sim 0.4$ $cm^2/V\cdot s$ and on/off ratios larger than 10^4 .

EXAMPLE 7

5 By tailoring the resistivity of ZnO films from semiconducting to semi-insulating, as shown in Fig. 1, a transparent thin film transistor was fabricated using only ZnO. The substrates were glass and polyethylene terephthalate (PET). Source-drain electrodes of conducting ZnO were first grown by sputtering at 100 W from a ZnO target in 10 mTorr of Ar without
10 oxygen. The semiconducting channel layer, 100 nm thick, was then sputtered at 20 mTorr Ar and 1×10^{-5} Torr of O₂. The next layer was a semi-insulating ZnO for the gate dielectric, 500 nm thick, made by sputtering a ZnO target in a 50% mixture of Ar+O₂ at a total pressure of 10 mTorr. Finally the ZnO gate electrode was sputtered at the same
15 conditions used for the source-drain electrodes. As shown in Figure 10, this structure is optically transparent, allowing easy reading of the caption, "ZnO TFT" beneath the transistor. The current-voltage characteristic in Figure 11 illustrates that the source-drain current can be modulated by an application of a gate voltage.

20

EXAMPLE 8

Using the transistor configuration shown in Fig. 3, an indium oxide thin film semiconductor was rf magnetron sputtered at room temperature to deposit
25 between source and drain electrodes, using a shadow mask. The indium oxide target was 6.5 inch diameter and the rf power for sputtering was 100 W. The total gas pressure during sputtering was 12 mTorr, comprised of 2 mTorr of oxygen, or pO₂ close to P_c, with the balance of 10 mTorr argon. The indium oxide film thickness, determined optically, was 1285 Å for a
30 sputtering time of about 33 min. Fig. 12 is a set of corresponding drain current (I_d) versus drain voltage (V_d) transistor curves for gate voltages (V_g) between -20 V and 10 V. For this device, the field effect mobility (μ_{FE}) from the linear current-voltage characteristics was determined to be

17 $\text{cm}^2/\text{V-s}$ with an on/off ratio equal to about 2×10^2 . This on/off ratio can likely be improved by use of a higher gate voltage and optimization of sputtering conditions.

5

EXAMPLE 9

This example illustrates low voltage and high current operation in a ZnO TFT on an aluminum oxide gate dielectric. The substrate, which also served as the gate electrode, was a heavily doped (with Phosphorous), n-type silicon wafer, 1-inch x 1-inch x 475 microns thick. One side of this wafer was coated with an aluminum oxide gate dielectric layer by electron-beam evaporation from a high purity, solid aluminum-oxide source. The measured aluminum oxide film thickness was 4483 Å. Aluminum-metal source and drain electrodes, about 1500 Å thick, were thermally evaporated on the oxide dielectric through a shadow mask to create a transistor channel length 80 microns by about 800 microns wide. A shadow mask was then used to magnetron sputter ZnO semiconductor, 918 Å thick, in the channel between source and drain electrodes. Sputtering was in 20 mTorr Ar and 1×10^{-5} Torr O_2 . Figure 13 is a set of transistor current (I_d) versus drain voltage (V_d) curves for gate voltages between zero and three (3) volts and V_d between 0 and 3 V. For this device the field-effect mobility was determined to be $\sim 3 \text{ cm}^2/\text{V-s}$ with an on-off ratio $> 10^3$. For three volt operation the current is substantial at > 1 microampere.

CLAIMS

1. A process for depositing undoped transparent oxide semiconductors,
5 selected from the group consisting of zinc oxide, indium oxide, tin oxide,
and cadmium oxide, in a field effect transistor, comprising a method
selected from the group consisting of :
 - a) physical vapor deposition of undoped TOS in an effective partial
pressure of oxygen mixed with an inert gas;
 - 10 b) resistive evaporation of undoped TOS in an effective partial
pressure of oxygen;
 - c) laser evaporation of undoped TOS in an effective partial
pressure of oxygen;
 - d) electron beam evaporation of undoped T-OS in an effective
15 partial pressure of oxygen; and
 - e) chemical vapor deposition of undoped T-OS in an effective
partial pressure of oxygen.
2. The process of Claim 1 where the physical vapor deposition is rf
20 magnetron sputtering.
3. The process of Claim 1 where the physical vapor deposition is dc
magnetron sputtering.
- 25 4. The process of Claim 1 where the physical vapor deposition is diode
sputtering.
5. The process of Claim 1 where the physical vapor deposition is triode
sputtering.
30
6. The process of Claim 1 where the physical vapor deposition is ion
beam sputtering.

7. The process of any of claims 1(a), 2, 3, 4, 5 or 6 wherein deposition is by physical vapor deposition and wherein the inert gas is selected from the group consisting of helium, neon, argon, krypton, and xenon.
8. The process of Claim 1(e) wherein the chemical vapor deposition is low pressure chemical vapor deposition.
9. The process of Claim 1(e) wherein the chemical vapor deposition is plasma-enhanced chemical vapor deposition.
10. The process of Claim 1(e) wherein the chemical vapor deposition is laser-enhanced chemical vapor deposition.
11. The process of Claim 1(e) where the chemical vapor deposition is atomic layer chemical vapor deposition.
12. The process of any one of claims 1 to 11 wherein the effective partial pressure of oxygen is between 0.1 and 10 times the critical pressure.
13. The process of any one of claims 1 to 11 wherein the effective partial pressure of oxygen is between 0.5 and 2 times the critical pressure.
14. A transistor comprising an undoped transparent oxide semiconductor.
15. A transistor comprising a transparent oxide semiconductor made by a process selected from the group of process consisting of the process as of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13.
16. A flat panel display comprising one or an array of transparent oxide semiconductor transistors as described by Claim 14.

17. An active matrix imager comprising an array of transparent oxide semiconductor transistors as described by Claim 14.
18. A sensor comprising an array of transparent oxide semiconductor
5 transistors as described by Claim 14.
19. A rf price label comprising an array of transparent oxide semiconductor transistors as described by Claim 14.
- 10 20. A rf identification tag comprising an array of transparent oxide semiconductor transistors as described by Claim 14.
21. A rf inventory tag comprising an array of transparent oxide semiconductor transistors as described by Claim 14.
- 15 22. The transistor of Claim 14 deposited on a flexible substrate.
23. The transistor of Claim 14 or Claim 15 further comprising source, drain and gate electrodes fabricated from a material selected from the
20 group consisting of zinc oxide, indium oxide, tin oxide, and cadmium oxide.
24. The transistor of Claim 22 further comprising a gate dielectric fabricated from a material selected from the group consisting of zinc oxide,
25 indium oxide, tin oxide, and cadmium oxide.

1/13

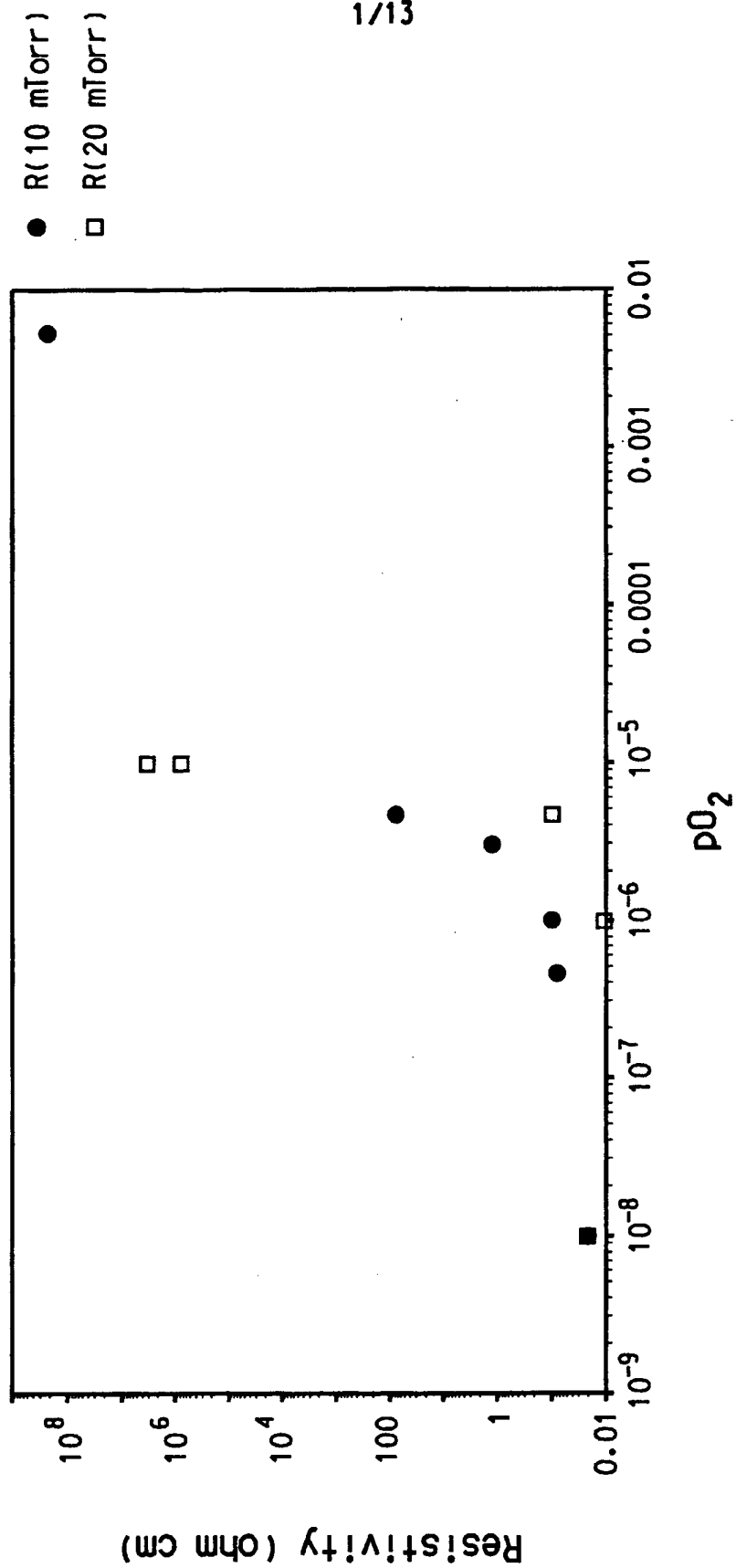


FIG. 1

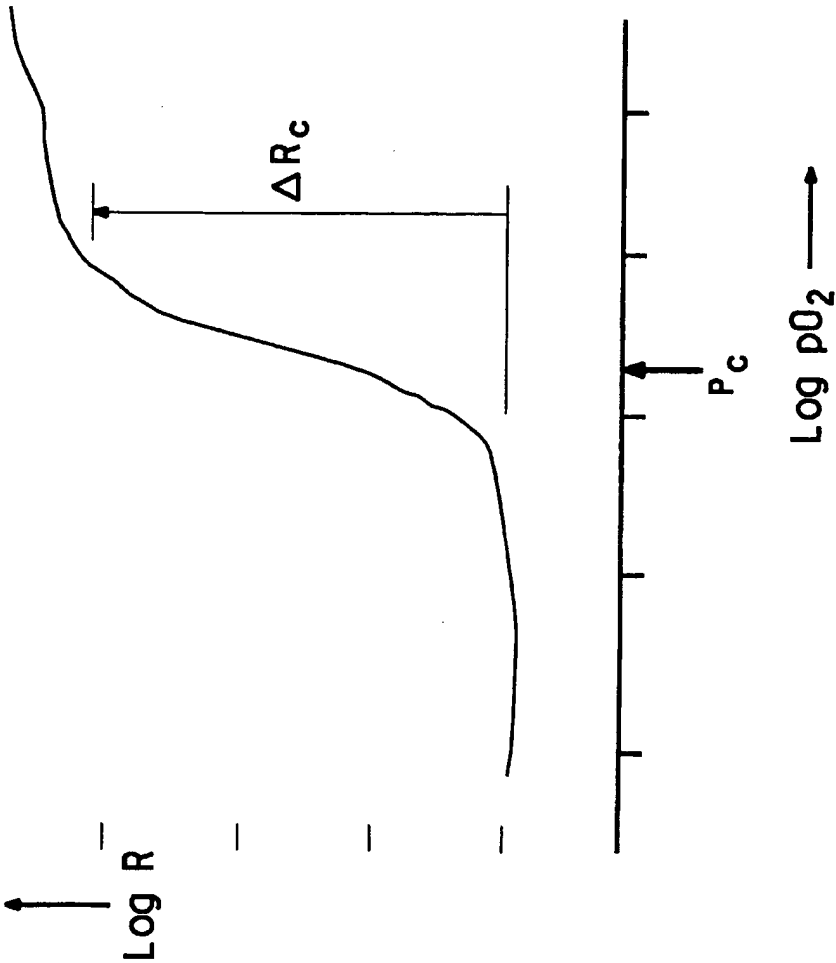


FIG. 2

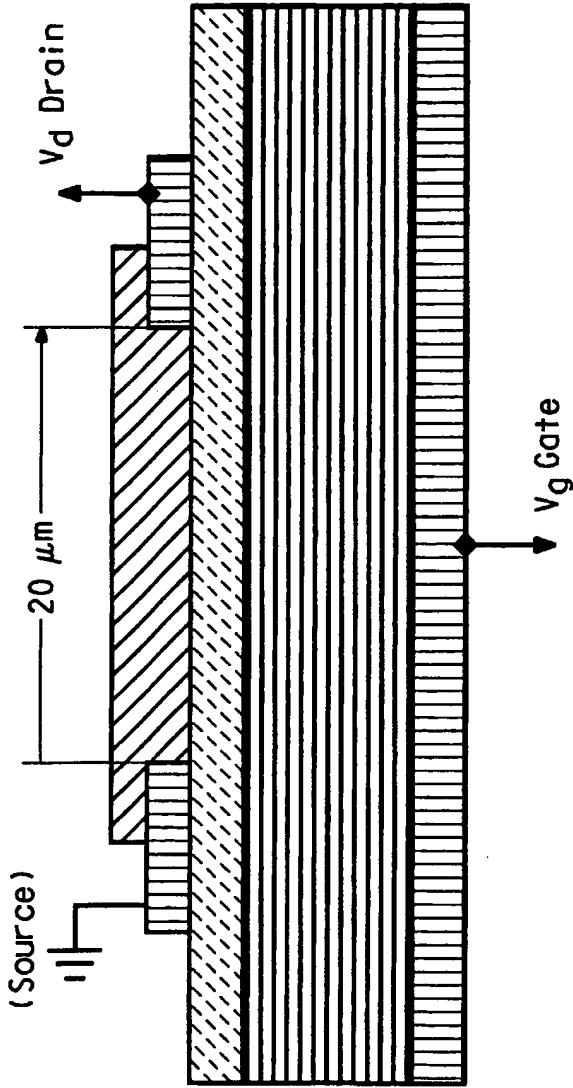
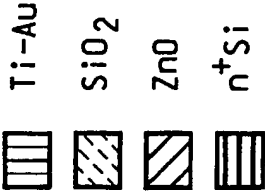


FIG. 3

4/13

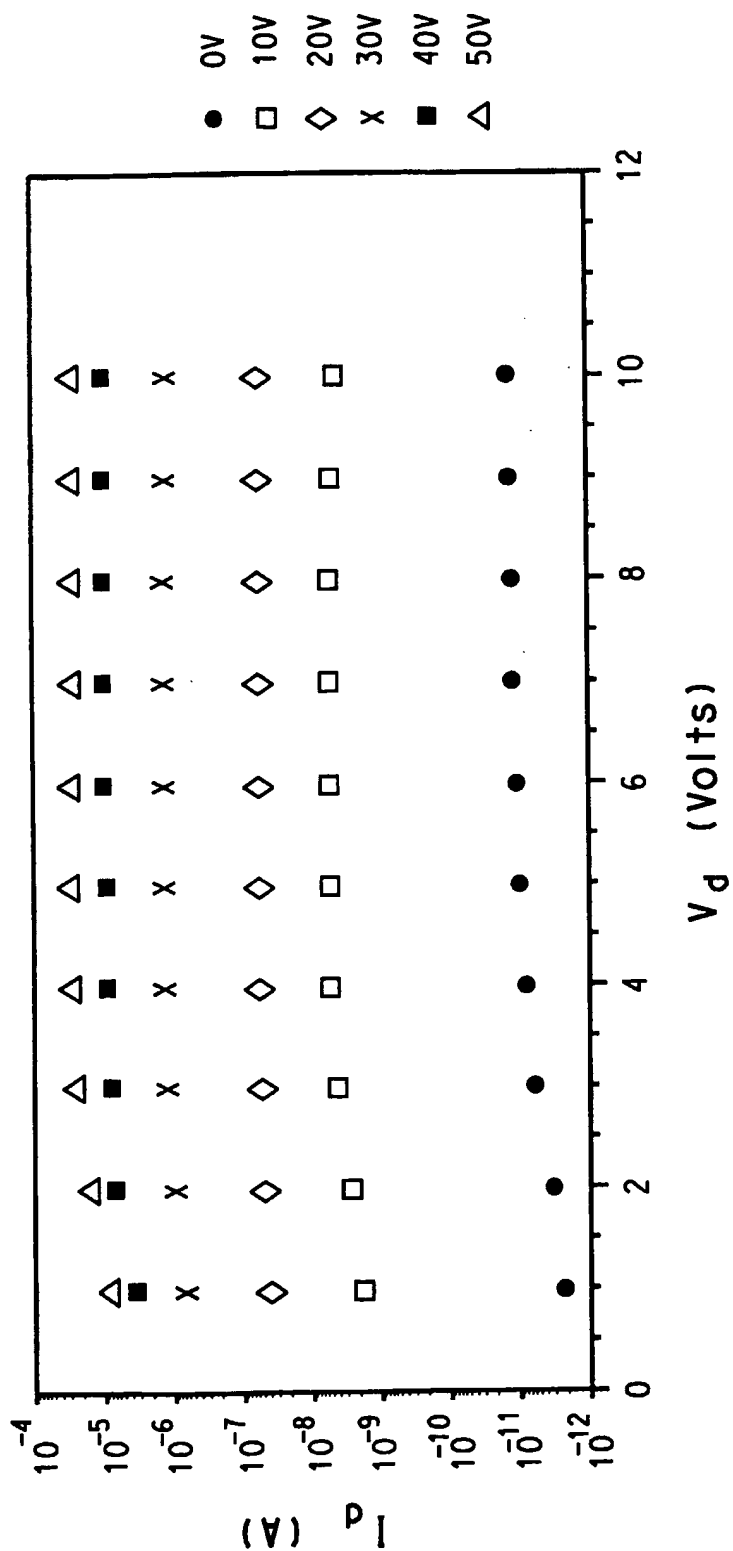


FIG. 4

5/13

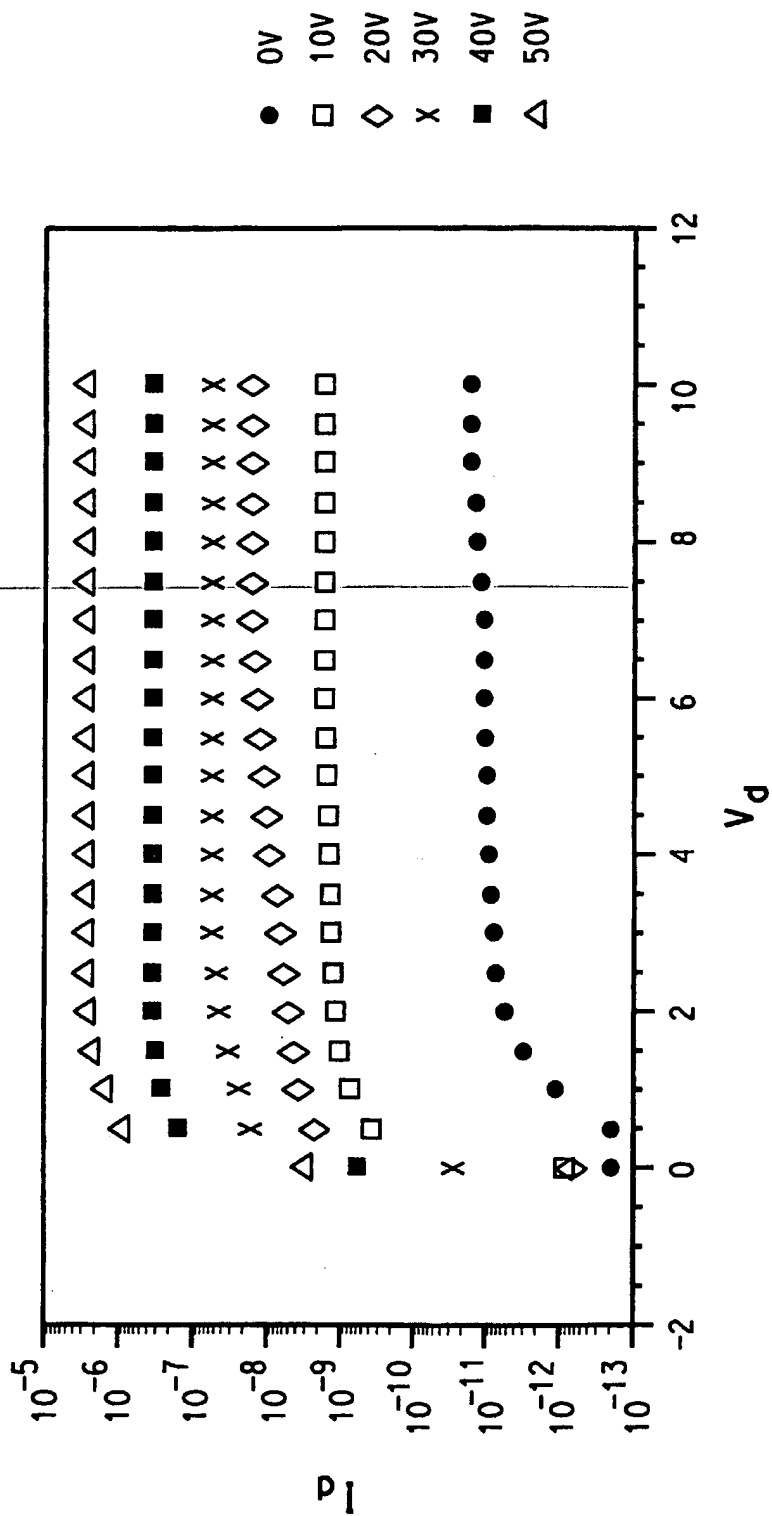


FIG. 5

6/13

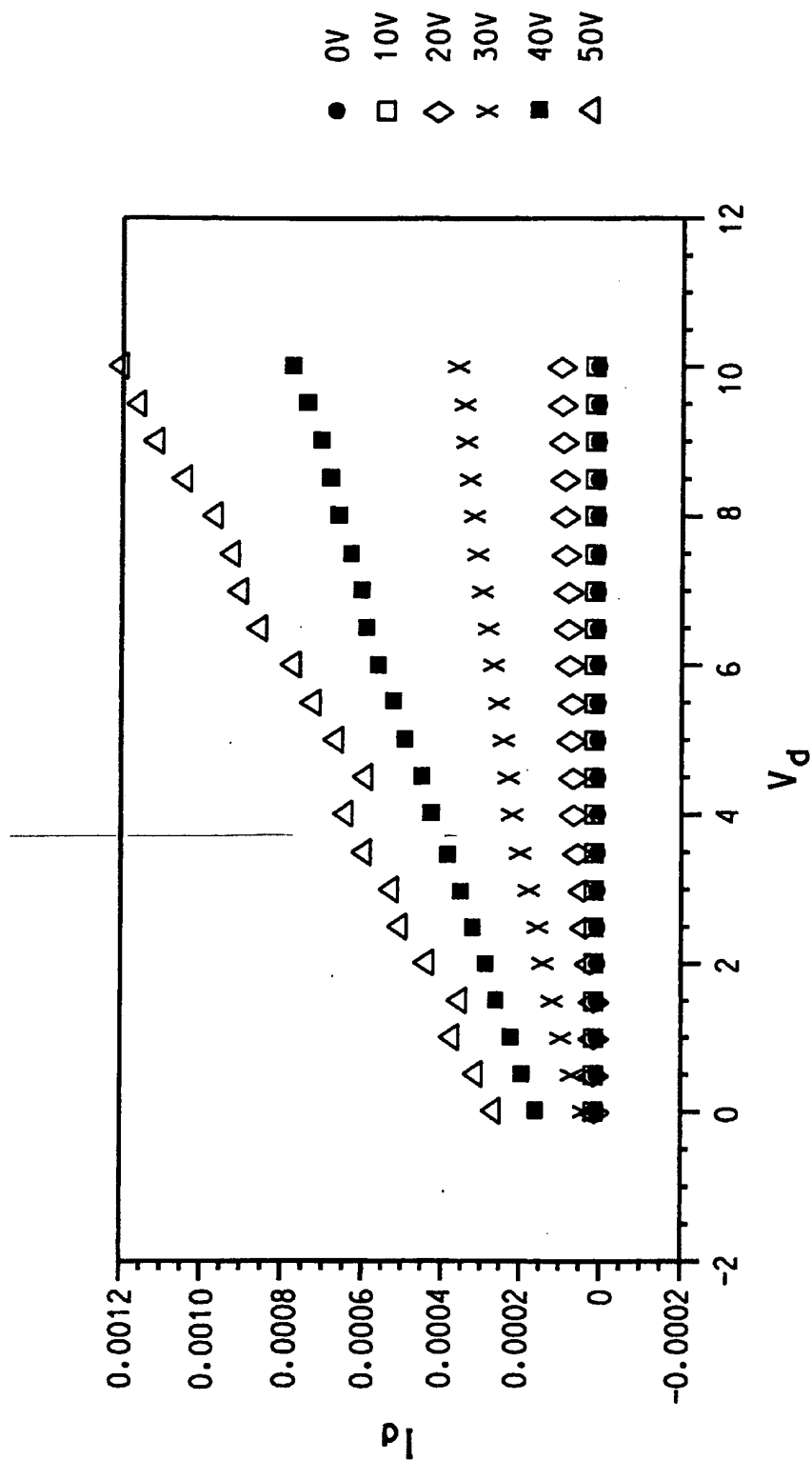


FIG. 6

7/13

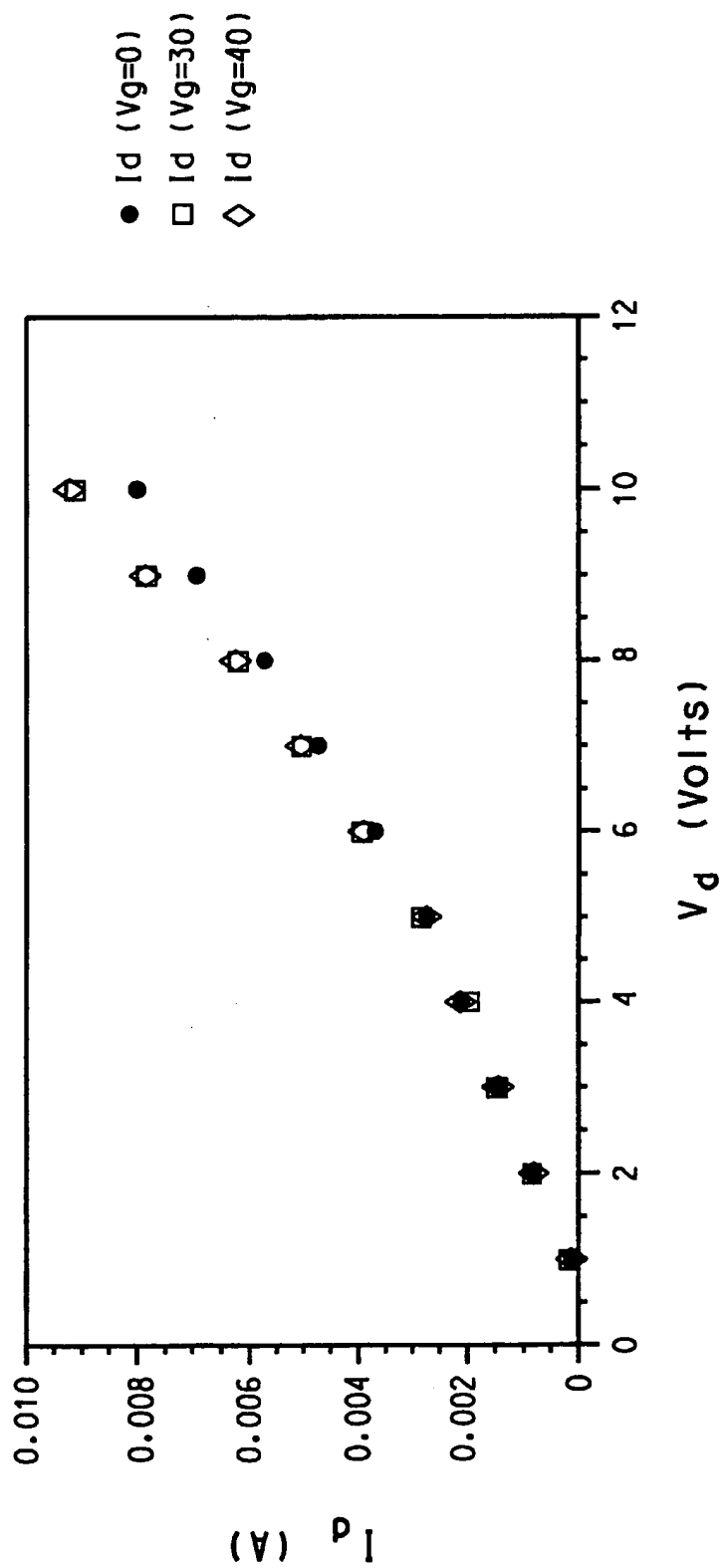


FIG. 7

8/13

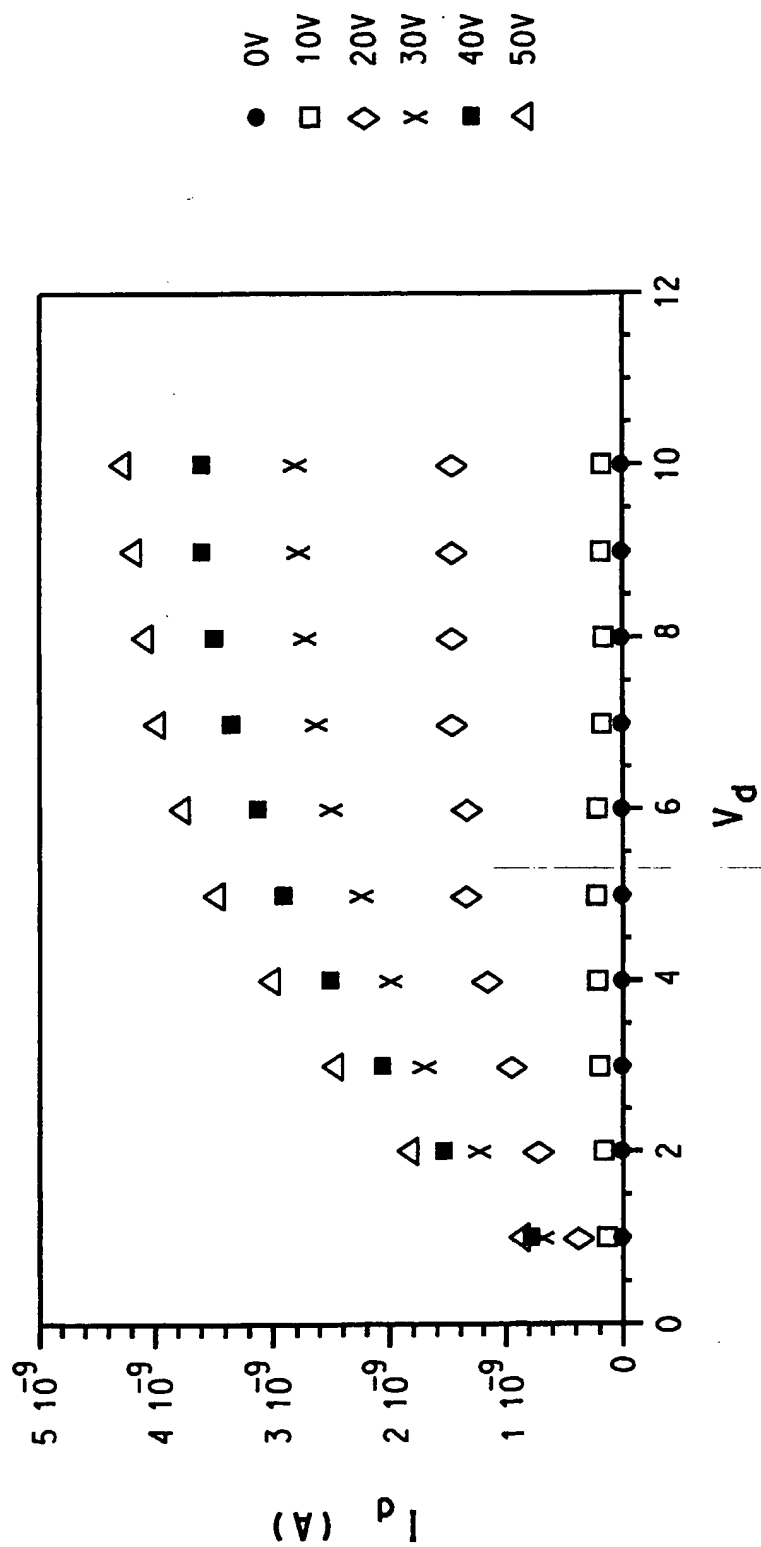


FIG. 8

9/13

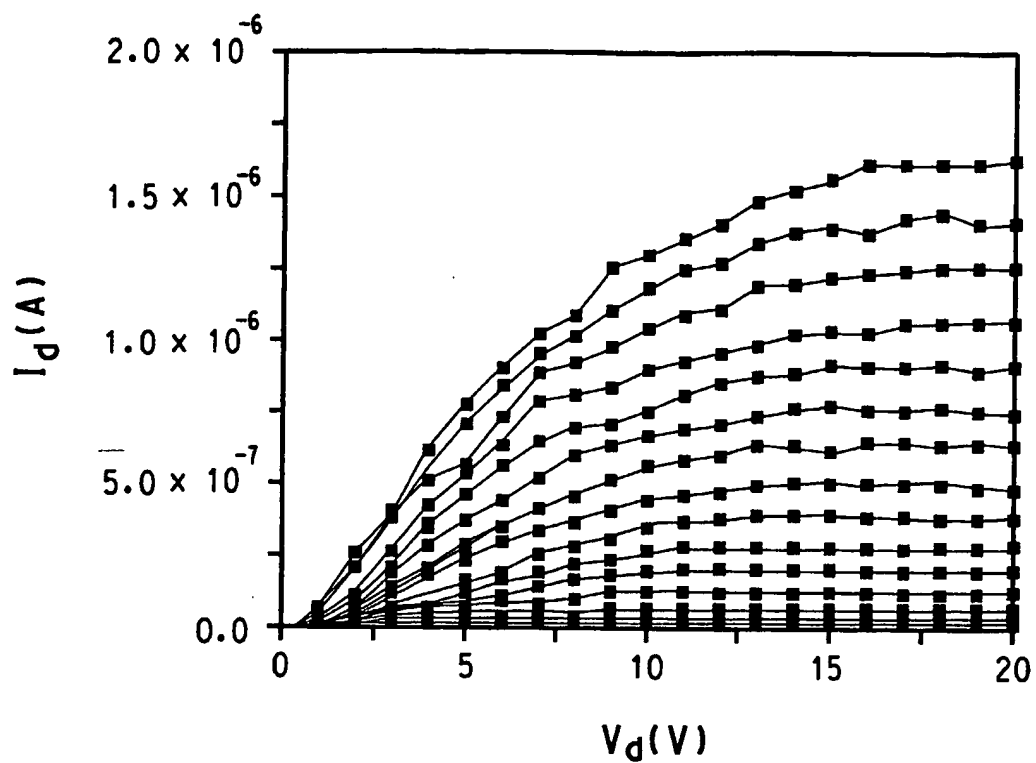


FIG. 9A

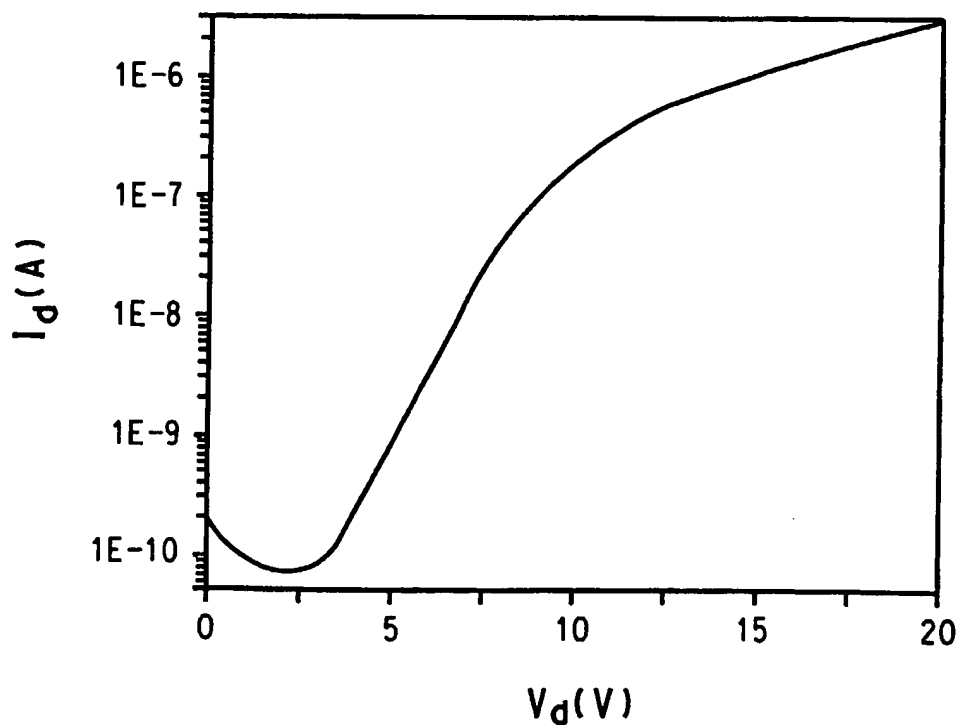


FIG. 9B

10/13

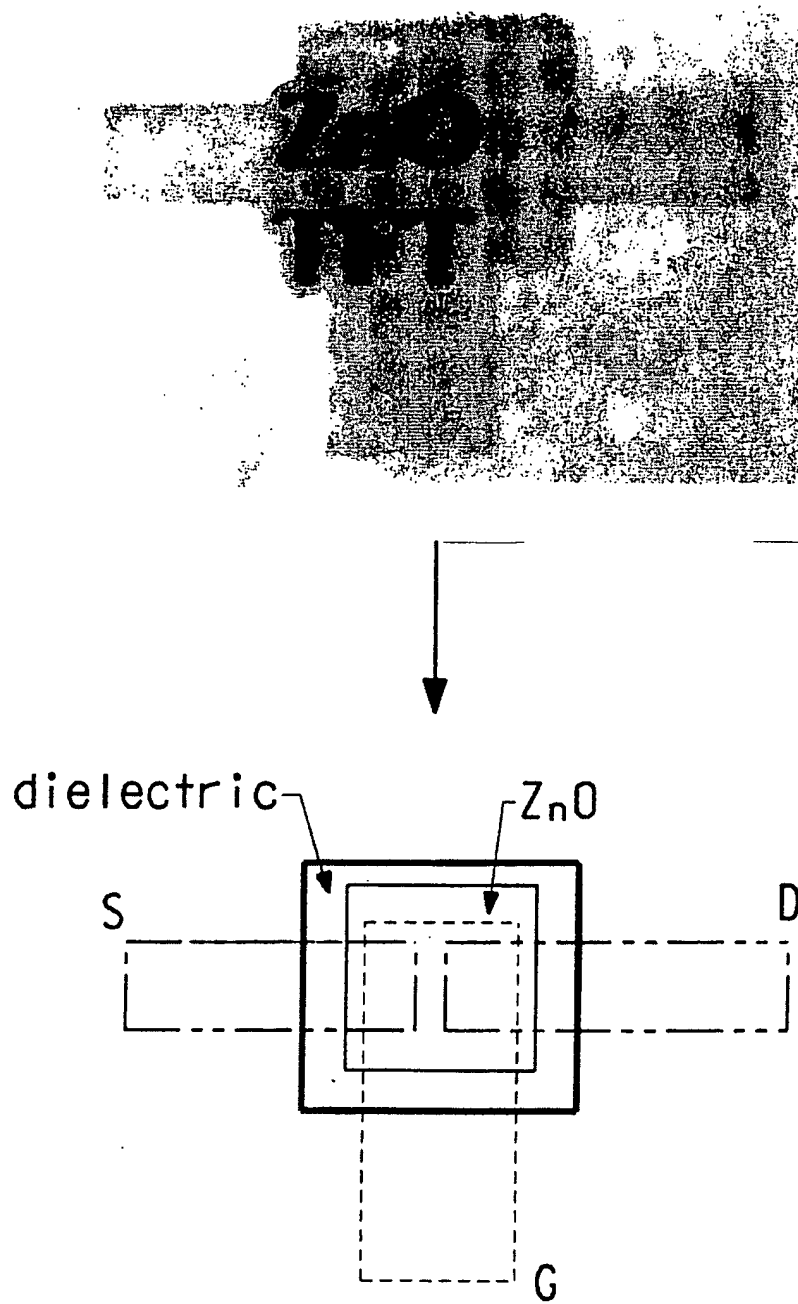


FIG. 10

11/13

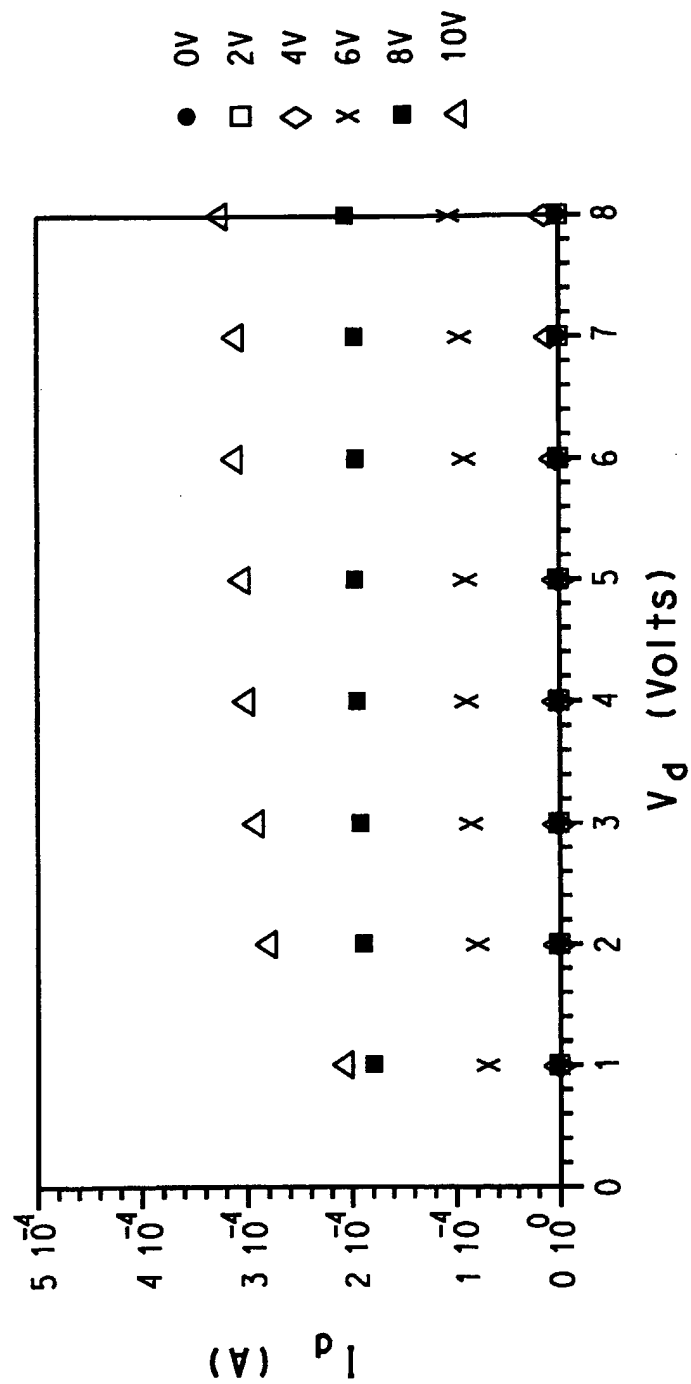


FIG. 11

12/13

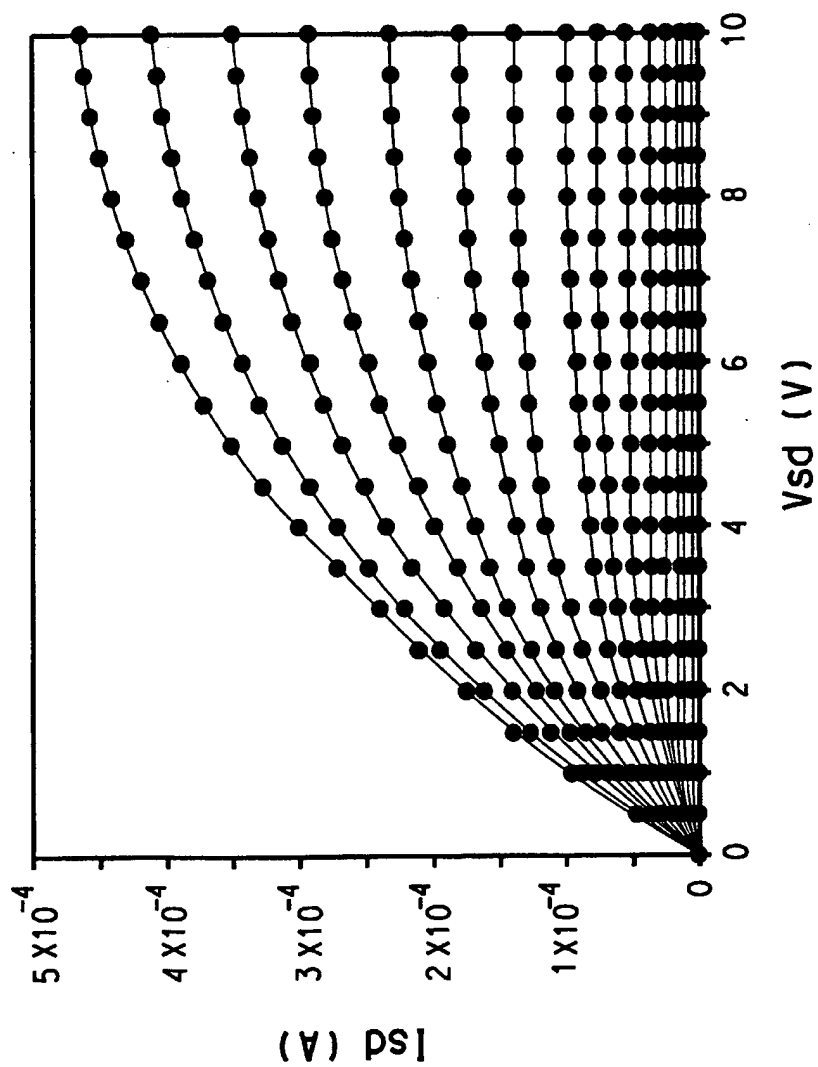


FIG. 12

13/13

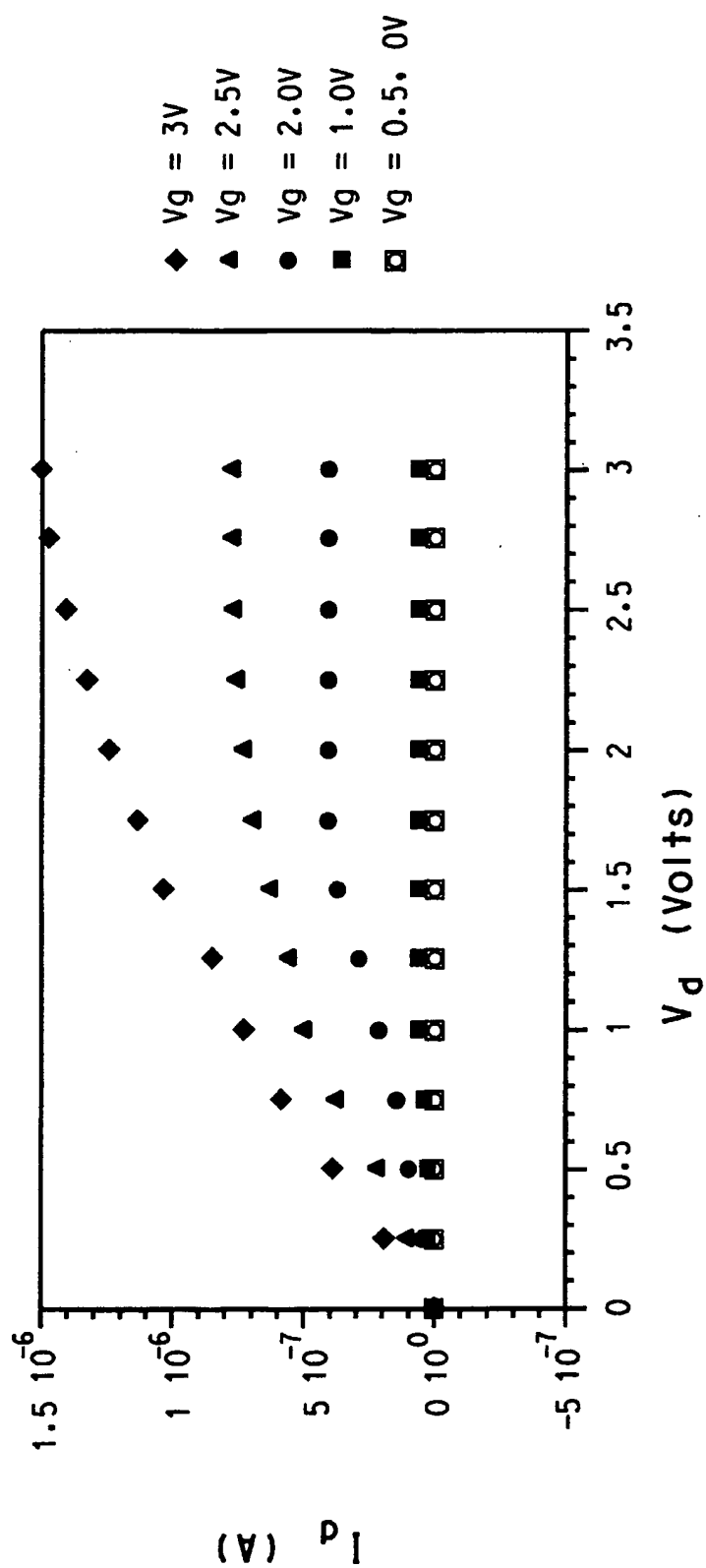


FIG. 13

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/034449 A3

(51) International Patent Classification⁷: **H01L 21/363**,
21/365, 29/24

(74) Agent: SIEGELL, Barbara, C.; E.I. Dupont De Nemours
and Company, Legal Patent Records Center, 4417 Lan-
caster Pike, Wilmington, DE 19805 (US).

(21) International Application Number:
PCT/US2003/032439

(22) International Filing Date: 10 October 2003 (10.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/417,767 11 October 2002 (11.10.2002) US

(71) Applicant (for all designated States except US): E.I. DU
PONT DE NEMOURS AND COMPANY [US/US]; 1007
Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CARCIA, Peter,
Francis [US/US]; 3413 Sweet Briar Road, Wilmington,
DE 19810 (US). MCLEAN, Robert, S. [US/US]; 208
Eileen's Way, Hockessin, DE 19707 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

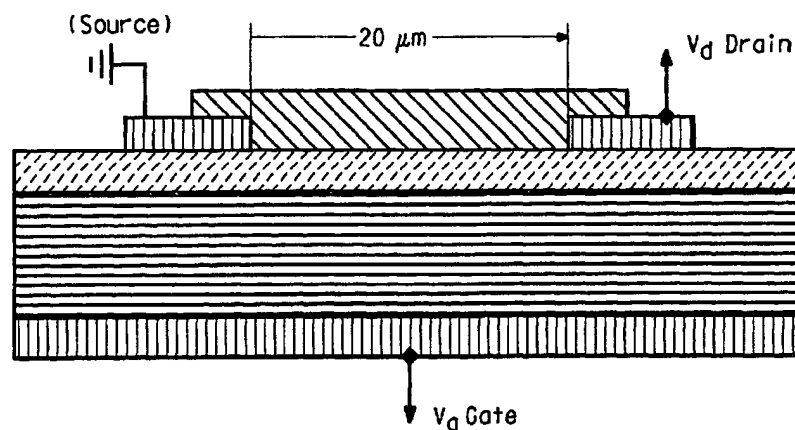
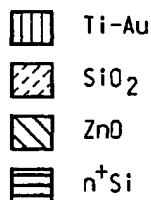
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

[Continued on next page]

(54) Title: TRANSPARENT OXIDE SEMICONDUCTOR THIN FILM TRANSISTORS



(57) Abstract: This invention relates to novel, transparent oxide semiconductor thin film transistors (TFT's) and a process for making them.

WO 2004/034449 A3



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(88) Date of publication of the international search report:
14 October 2004

INTERNATIONAL SEARCH REPORT

PCT /US 03/32439

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/363 H01L21/365 H01L29/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OHTOMO A ET AL: "NOVEL SEMICONDUCTOR TECHNOLOGIES OF ZNO FILMS TOWARDS ULTRAVIOLET LEDS AND INVISIBLE FETS" IEICE TRANSACTIONS ON ELECTRONICS, INSTITUTE OF ELECTRONICS INFORMATION AND COMM. ENG. TOKYO, JP, vol. E83-C, no. 10, October 2000 (2000-10), pages 1614-1617, XP000970183 ISSN: 0916-8524	1, 14-21, 23
Y	pages 1614 and 1617 ----- -/--	2-13, 22, 24

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

28 July 2004

Date of mailing of the international search report

11/08/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Wolff, G

INTERNATIONAL SEARCH REPORT

PCT /US 03/32439

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	S. MANIV, C.J. MINER, W.D. WESTWOOD: "Transparent conducting zinc oxide and indium-tin oxide films prepared by modified reactive planar magnetron sputtering" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY A, vol. 1, no. 3, 1983, pages 1370-1375, XP001182598 cited in the application	1,14-16, 18,23
Y	Abstract, I. INTRODUCTION, II. EXPERIMENTAL, IV. CONCLUSION; table III -----	2-13
X	HAARTSEN J C ET AL: "The junction FET used as a SAW detector in ZnO-SiO ₂ -Si structures" PROCEEDINGS OF THE IEEE 1989 ULTRASONICS SYMPOSIUM, 3 October 1989 (1989-10-03), pages 207-211, XP010090586	1,14-16, 18,23
Y	I. INTRODUCTION, II. THE JFET DETECTOR, III. TECHNOLOGY; figure 1 -----	24
Y	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 07, 3 July 2002 (2002-07-03) & JP 2002 076356 A (JAPAN SCIENCE & TECHNOLOGY CORP), 15 March 2002 (2002-03-15) cited in the application abstract	14-24
X	OHYA Y ET AL: "THIN FILM TRANSISTOR OF ZNO FABRICATED BY CHEMICAL SOLUTION DEPOSITION" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 40, no. 1, PART 1, January 2001 (2001-01), pages 297-298, XP001001679 ISSN: 0021-4922 cited in the application first paragraph	14-23
X	S. GIANCATERINA ET AL.: "Elaboration and adhesion of zinc oxide coatings on poly-ether-ether-ketone films" SURFACE AND COATINGS TECHNOLOGY, vol. 138, 2001, pages 84-94, XP001182596 cited in the application	1-7,12, 13
Y	Abstract, 2. Experimental details -----	14-24
	----- -/--	

INTERNATIONAL SEARCH REPORT

PCT /US 03/32439

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>E. FORTUNATO ET AL.: "Characterization of Zinc Oxide Thin Films Deposited by rf Magnetron Sputtering on Mylar Substrates" MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS, vol. 666, 2001, pages F3.21.1-F3.21.6, XP009034453 cited in the application INTRODUCTION, EXPERIMENTAL DETAILS -----</p>	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT /US 03/32439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2002076356 A	15-03-2002	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.